Quantum Chemical Study of Mechanisms for Oxidative Dehydrogenation of Propane on Vanadium Oxide

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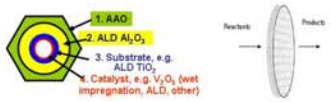
Introduction

- **Motivation:** Advance molecular-level understanding and control of pathways for selective catalytic oxidation through experiment and theory
- **Catalytic material:** A new and unique architecture for supported membrane catalysts using atomic layer deposition and anodized aluminum oxide (talk by Peter Stair)
- **Catalytic reactions:** Selective oxidative dehydrogenation (ODH), which is an important class of catalytic reaction used in industry
- **Major Question:** What is the role of support in the catalytic reaction and how to improve efficiency?

Computational Methods

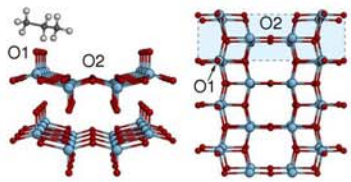
- **Cluster Models:** Used to model multi-step reactions on local sites; up to 50 atoms included in cluster
- **Periodic Models:** Use to include crystalline environment
- **Ab initio molecular orbital theory:** Methods such as G3 theory (developed at Argonne) used to obtain very accurate energies on small clusters
- **Density functional theory:** Hybrid methods such as B3LYP used for larger clusters and periodic calculations

Joint with experimental program on atomic level control of nanoporous membranes for catalysis

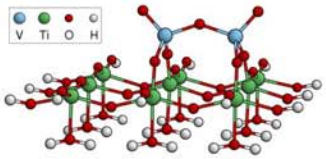


One-pass-through catalytic conversion using a nanoporous membrane (see poster of Pellin et al.)

Models for Catalytic Sites

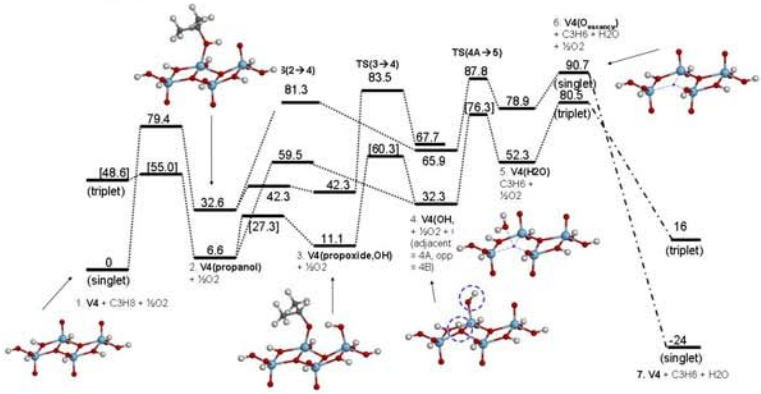


V_2O_5 (010) surface

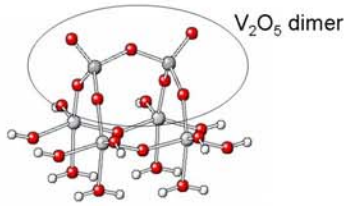


Vanadia cluster on TiO_2 substrate

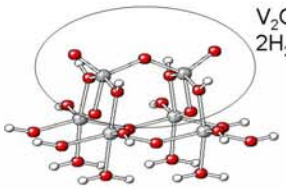
Propane reaction (energies in kcal/mol) at vanadyl site (O1) on V_2O_5 (010) surface: large barriers (>75 kcal/mol)



Propane insertion into vanadia cluster on a TiO_2 support: reduced cluster shows dramatic decrease in barrier



Formal V charge: +5
Barrier: 70 kcal/mol
Reaction energy: 16 kcal/mol



Formal V charge: +3
Barrier: 31 kcal/mol
Reaction *energy: -12 kcal/mol*

Major Findings

- Multi-step reaction mechanism has large barriers on a V_2O_5 surface (75-90 kcal/mol)
  - Barriers are much larger than expected from experiment
- Support stabilizes reduced, hydroxylated, clusters that provide reactive sites for propane
  - Lower barriers that are in agreement with experiment

Future work on molecular level understanding of catalytic reactions

- Investigation of dependence on catalytic cluster size and support material
- Incorporate structure of nanoporous membranes from MD simulations (see poster of Adiga et al.)
- Maintain close coordination with future experimental studies on similar systems (example: look for hydrogens on surface)

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